

Charge-transfer exciton in La_2CuO_4 probed with resonant inelastic x-ray scattering

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We report a high-resolution resonant inelastic x-ray scattering study of La_2CuO_4 . A number of spectral features are identified that were not clearly visible in earlier lower-resolution data. The momentum dependence of the spectral weight and the dispersion of the lowest energy excitation across the insulating gap have been measured in detail. The temperature dependence of the spectral features was also examined. The observed charge transfer edge shift, along with the low dispersion of the first charge transfer excitation are attributed to the lattice motion being coupled to the electronic system. In addition, we observe a dispersionless feature at 1.8 eV, which is associated with a d-d crystal field excitation.

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As the prototypical parent insulating compound, La_2CuO_4 has drawn much attention as a starting point for the study of high-temperature superconductors. La_2CuO_4 is well described as an antiferromagnetic insulator with a $d_{x^2-y^2}$ hole localized at the Cu site due to the strong electron correlations. In particular, this material is classified as a charge-transfer (CT) insulator, since the lowest energy charge excitation across the insulating gap corresponds to transferring an electron from oxygen to a neighboring copper. This CT excitation creates a Cu^{1+} ion and an oxygen 2p hole that forms a Zhang-Rice singlet (ZRS) with the neighboring copper spin, the two copper sites forming a bound state [1]. Over the years, exciton formation of these electron-hole pairs has been considered by several authors as a possible low energy elementary excitation in this half-filled copper oxide plane [2, 3, 4, 5, 6, 7, 8]. The strong magnetic interaction in this system has been pointed to as the origin of the exciton binding energy [2] as well as the large dispersion of the excitation [4]. Indeed the apparently large dispersion observed in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ using electron energy loss spectroscopy (EELS) was attributed to a CT exciton with a small effective mass [9].

Experimentally, optical spectroscopy and Raman scattering studies have been carried out to address the nature of the excitation spectrum near this CT gap [10, 11, 12, 13]. Ohana et al. directly observed the coupling of the electronic excitations to the lattice system in the resonance of phonon Raman lines at laser energies around the CT energy (2.14 eV) and a low-energy shoulder at 1.9 eV [10]. Falck et al. found that a polaron model was able to reproduce their reflectivity data very well for a wide temperature range [11]. However, despite extensive experimental and theoretical studies to date, the nature of the CT exciton is still controversial. Outstanding questions include whether the electron-hole pair

actually form a bound exciton state, or if they remain as a resonance state within the particle-hole continuum. Another question relates to the relative role played by magnetic interactions and/or phonons in the exciton formation and dispersion. For each of these questions, valuable information can be gained by studying the momentum dependence of the charge transfer excitations. In recent years, resonant inelastic x-ray scattering (RIXS) has drawn considerable interest as a valuable spectroscopic tool for studying the momentum-dependence of various electronic excitations in insulating cuprates such as these excitons [14, 15, 16, 17, 18, 19, 20, 21]. However, these earlier studies have been hampered by relatively poor instrumental energy resolution.

In this Letter, we report detailed studies of electronic excitations near the CT gap in the prototypical cuprate compound, La_2CuO_4 , using the highest energy resolution to date for RIXS, 130 meV (full-width at half-maximum). We observe several new features which were previously not clearly visible. We find that 1) the RIXS spectra are composed of multiple spectral features which exhibit complex dispersion and spectral weight change as a function of momentum transfer; 2) the two lowest energy features observed correspond to a dispersionless dd-excitation at 1.8 eV and a CT exciton at 2.2 eV; 3) the latter disperses with a bandwidth of ~ 0.3 eV in the $(\pi, 0)$ direction and of at least that much along (π, π) where its intensity decreases rapidly as one goes from the zone centre towards (π, π) and 4) the edge of the CT excitation shifts to lower energy for increased temperatures in accordance with previous optical studies [11]. We argue that these results are consistent with a picture of a bound exciton state in the presence of strong e - ph coupling.

The RIXS experiments were carried out at the Advanced Photon Source on the undulator beamline 9IDB. A detailed description of the experimental setup was re-

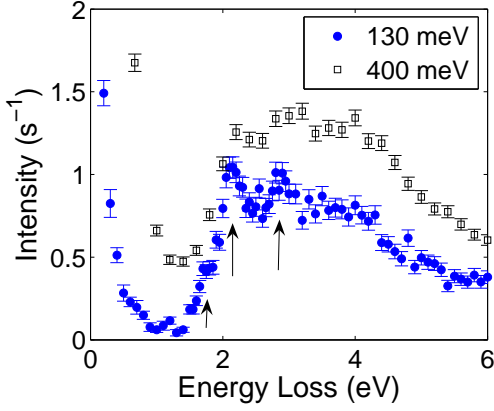


FIG. 1: (Color online) Comparison of RIXS spectra obtained using 400 meV resolution (squares, from Ref. [18]) and meV resolution (circles) used in the present work. The meV spectrum has been scaled by a factor of 1/5 to be comparable inelastic intensity with the 130 meV spectra

ported in Ref. [22]. The floating-zone grown La_2CuO_4 sample was cooled to 27 K by a closed cycle refrigerator to reduce the phonon contribution to the background. We used the same experimental geometry as that used in Ref. [18].

The improvement in energy resolution is clearly visible in Fig. 1, in which we compare the RIXS spectra of La_2CuO_4 obtained with two different resolutions. The open square symbols represent data taken from Ref. [18], obtained with 400 meV resolution, while the filled circles represent the new data obtained with 130 meV resolution. Both spectra were measured with the same incident energy ($E_i = 8992$ eV) [23] and momentum transfer $\mathbf{Q}=(3\ 0\ 0)$ in tetragonal notation. Note that the tail of the elastic line is drastically reduced in the energy range below 2 eV. Although the overall shapes of the spectral features are almost identical, the improved energy resolution allows us to see several sharp features in the spectrum. Specifically, one can identify a sharp peak at the energy corresponding to the CT gap of this material at 2.2 eV, and several spectral features at higher energies, including a prominent peak at 2.9 eV. These features have been observed in a recent study by Lu et al. [21], where the incident energy was varied to elucidate the different peaks. In addition, a low-energy shoulder of the main peak is, for the first time at $\mathbf{q}=0$, resolved at around 1.8 eV (this feature has been recently observed near the zone boundary [20]). Since the overall incident energy dependence of the spectral features at zero momentum transfer was found to be consistent with earlier studies [18], we focus our attention on the momentum dependence at fixed incident energy in the following.

To investigate the momentum dependence, energy loss scans were taken with the fixed incident energy at various reciprocal space points in the two high-symmetry directions: $(\pi,0)$ along the Cu-O bond, and (π,π) at a 45

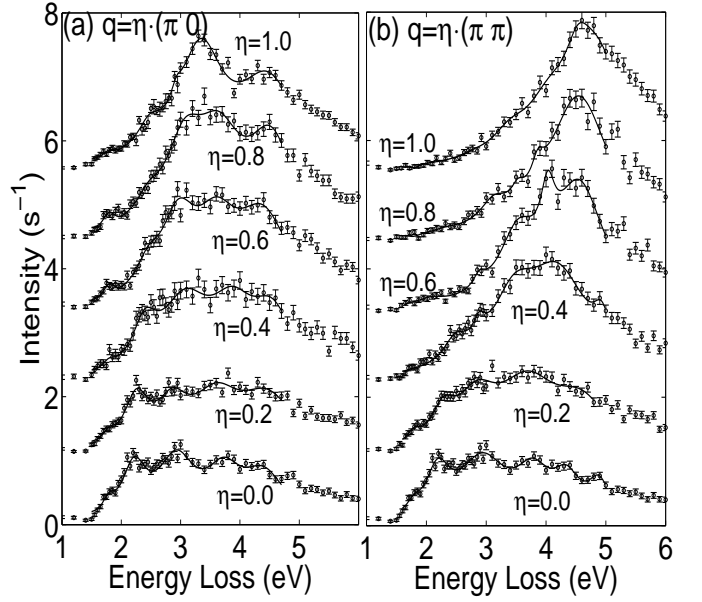


FIG. 2: Momentum dependence of the RIXS spectrum along the (a) $(\pi, 0)$ and (b) (π, π) directions. The incident energy is 8992.5 eV. All curves are normalized by the elastic peak intensity during each scan, and shifted along the intensity axis for clarity.

degree angle. Each scan was normalized by the intensity of the elastic peak. Figure 2 shows the development of the spectra as the momentum transfer \mathbf{q} increases away from zone center. The zone boundary scans at $(\pi,0)$ and (π,π) look similar to earlier low-resolution data; that is, there exist two well defined peaks at $(\pi,0)$, while only one prominent peak appears at (π,π) . The progression of the spectral features as a function of momentum transfer involves both actual shifts of the peak positions as well as intensity changes in the respective peaks. In order to analyze the dispersion quantitatively, the spectra were fit to multiple Lorentzian peaks (solid lines in Fig. 2).

The results of the fits for the two lowest energy features are shown in Fig. 3. The salient feature of the 1.8 eV peak is its lack of energy dispersion, which suggests that this excitation is spatially localized. The most likely candidate for this excitation is a crystalline-field dd excitation. We note that charge transfer with the surrounding $O2p$ states of the same symmetry would also be involved [8, 13]. This peak assignment is consistent with earlier studies using different experimental techniques, such as large-shift Raman scattering [13], Cu M-edge RIXS [24], and L-edge RIXS [26]. In addition, the 1.8 eV shoulder was also observed near the zone boundary in a recent K-edge RIXS study [20], and likewise attributed to a crystal field excitation. It is interesting to note that the dd -excitation is much stronger than the CT excitation (at 2.2 eV) in the L-edge spectra, and vice versa in our K-edge spectra. Since the intermediate state of the L-edge RIXS directly involves Cu d -orbitals, it would have

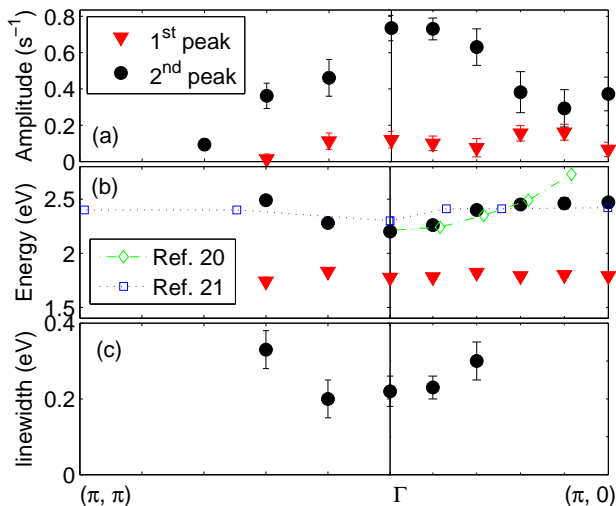


FIG. 3: (Color online) Momentum dependence of fitting parameters: (a) Spectral weights, (b) center positions, and (c) Lorentzian widths (FWHM). Due to the vanishing spectral weights, the energies and widths were only reliably determined until about half way across the Brillouin zone in the (π, π) direction. Included in the energy dispersion plot is a comparison with the results from other recent studies [20, 21]

large overlap with the final state of the dd -excitation, and generate large dd intensity as predicted by Tanaka et al. [27].

The next peak, corresponding to the main sharp feature at $\omega \sim 2.2$ eV in Fig. 1, was seen in previous RIXS and optical conductivity studies and widely associated with the excitation across the CT gap [28]. The dispersion of the CT excitation is shown in Fig. 3(b). A direct gap is exhibited, with a total bandwidth along the $(\pi, 0)$ direction of around 0.3 eV. This observation of a small bandwidth is in contrast to the earlier report of ~ 1 eV bandwidth observed with lower-resolution setup [18], but is consistent with the small bandwidth (≤ 0.5 eV) observed in more recent RIXS studies [19, 20, 21] as shown in Fig. 3(b). We note that our energies near $(\pi, 0)$ seem to match well with those of Ref. [21]. In contrast, the dispersion we observe matches very well with Ref. [20] from low q 's up to two thirds of the way towards the zone boundary, but then the two studies disagree for the last point of Ref. [20]. This is not entirely surprising, since the 2.2 eV peak loses intensity near the zone boundary and becomes a shoulder of the higher energy peaks, making energy determination more uncertain, especially in the case of lower resolution.

The observed bandwidth is in fact very close to that of the ZRS band of the insulating cuprates [30]. Along the (π, π) direction, the intensity of the 2.2 eV peak decreases, and the peaks eventually becomes unobservable around the halfway point across the zone. Similar dramatic momentum dependencies of the spectral weight have been predicted for certain CT excitons [4, 8]. We also note that

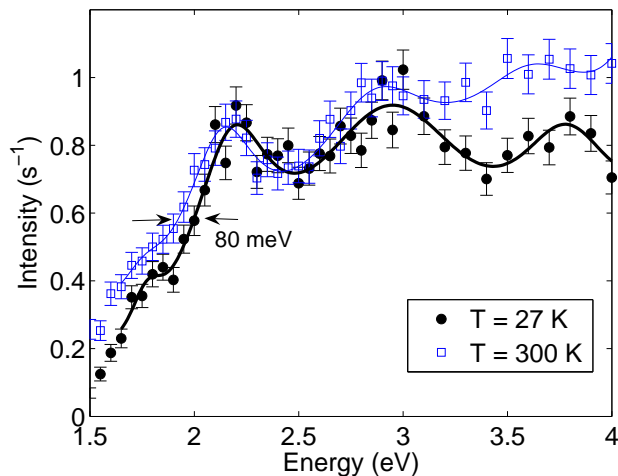


FIG. 4: (Color online) Comparison of the zone center spectra at $T = 27$ K and $T = 300$ K. The two spectra were scaled to match their intensities at 10 eV energy loss.

the peak width is not limited by resolution, and broadens as q increases, as shown in Fig. 3(c), suggesting that the excitation becomes less well-defined at larger momentum transfers. Such a result would be expected if there are more decay channels available at higher q .

We have also obtained the zone center spectrum at 300 K which is compared to the 27 K scan in Fig. 4. Since the elastic intensities vary at different temperatures, the two spectra were in this case scaled to match the intensities of their Cu $K\beta_5$ emission lines, which are at 10 eV. Note that the CT peak intensity also happens to match when this normalization scheme is used, which is appropriate for comparing shifts in the CT gap edge. A red shift of ~ 80 meV is seen in the CT gap edge, measured at $\omega = 2$ eV as shown in the figure. Sources of error in this shift determination include uncertainty in the energy loss scale, and possible incident energy variations between the two scans. The effect of the latter was found to be negligible; even for relatively large changes in the incident energy (500 meV), the fitted edge of the CT peak did not shift by more than 5 meV. One contribution to the error in energy loss scale between the two scans is the zero-loss reference, determined by fitting the elastic line, and is accurate to within 10 meV. Thus, we conclude that the observed shift is mostly due to the temperature change, and agrees with the ~ 100 meV shift observed in optical reflectivity measurements [11]. We would like to point out that although the RIXS spectrum has often been compared with the corresponding optical spectrum, it has been difficult to draw direct correlation between the features observed in the two spectroscopies. The same thermal behavior of the 2.2 eV peak from the RIXS and the reflectivity measurement [11] implies that these peaks have the same origin.

One of the outstanding questions is whether or not the 2.2 eV peak seen in these data indeed corresponds to a

two-copper-site, bound exciton as described by a Zhang-Ng-type model [4]. One might use the non-zero peak width, indicative of a relatively short lifetime, to argue against a bound exciton-type picture. However we argue that in fact a bound exciton is a good description of the data. As possible explanations for the finite peak width, we point to the possibility of multiple excitations within the instrumental resolution, or alternatively, intrinsic broadening mechanisms associated with the antiferromagnetic lattice [31]. A third possibility is that the observed broadening of the RIXS peak as q is increased could result from the unbinding of the exciton. In this proposed scenario, the exciton energy lies just below the upper Hubbard band. Increasing q causes the bound exciton to disperse into the electron-hole continuum, decreasing the lifetime of the exciton and broadening the associated peak. This picture is somewhat similar to the situation in the 1D system Sr_2CuO_3 (Fig. 2(b) Ref.[32]), but the bound exciton exists near the zone center in La_2CuO_4 . Note that the binding energy of this exciton must be very small, since a large increase of the photoconductivity was observed just above the gap [33]. With these possible explanations for the observed non-zero peak width, it is reasonable to suppose that the 2.2 eV peak is indeed the lowest-energy CT exciton.

The relatively small overall magnitude of the observed dispersion would be expected if the excitations are strongly coupled to phonons, which will give them a high effective mass. On the other hand, a purely electronic model with only magnetic degrees of freedom (such as that of Ref.[4]) predicts much larger dispersion than that observed, since singlet exciton propagation does not disturb a magnetically ordered spin background. Thus, our results support a picture in which the e - ph interaction plays an important role in the exciton dispersion. This is also consistent with the optical reflectivity study [11]. Presumably the same mechanism, namely a temperature dependent e - ph interaction is also responsible for the observed red-shift of the RIXS peak [34, 35].

Finally, the higher energy excitations are somewhat more difficult to interpret, given the large overlap with each other and uncertainties in the fitting, and we can provide at most speculations about them. However, there is a clear peak in Fig. 2 at 2.9 eV which shows little or no energy dispersion, and whose amplitude decreases along the (π, π) direction but not along $(\pi, 0)$, where it can be seen as a shoulder to the main peak at zone boundary. This could be the dispersionless $b_{1g}e_u(\pi)$ 2-center exciton discussed by Moskvin et. al. [8]. At the zone boundaries, there are strong peaks at 4.5 eV for $q=(\pi, \pi)$ and 3.3 eV for $q=(\pi, 0)$. The narrowing of the latter feature gives the appearance of neighboring modes drawing together as q approaches the zone boundary, likely involving strong interaction between the modes [8].

In summary, we have studied the electronic excitations near the charge transfer gap of La_2CuO_4 using high res-

olution resonant inelastic x-ray scattering, observing a dispersionless dd excitation at 1.8 eV, and a weakly dispersive CT exciton at 2.2 eV at the Brillouin zone center, as well as higher energy peaks. Away from the zone center, the CT exciton peak broadens and disperses to higher energy, while losing its spectral weight. Its observed bandwidth is similar to that of the ZRS [30], and is much smaller than previously reported values, but in accordance with recent studies [20, 21]. This small bandwidth of the exciton dispersion, as well as the observed temperature dependence, underscores the importance of the e - ph interaction in insulating cuprates. It is clear that further theoretical study of exciton behavior in the presence of strong e - ph interactions would be useful for quantitative understanding of the electron correlations in cuprates.

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- [1] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
- [2] D. G. Clarke, Phys. Rev. B **48**, 7520 (1993).
- [3] M. E. Símón, A. A. Aligia and C. D. Batista, Phys. Rev. B **54**, R3780 (1996).
- [4] F. C. Zhang and K. K. Ng, Phys. Rev. B **58**, 13520 (1998).
- [5] E. Hanamura, N. Trung Dan and Y. Tanabe, J. Phys.:Condens. Matter **12**, L345 (2000).
- [6] P. Wrobel and R. Eder, Phys. Rev. B **66**, 035111 (2002).
- [7] A. S. Moskvin et. al., Phys. Rev. B **65**, 180512 (2002).
- [8] A. S. Moskvin et. al., cond-mat/0507707 (2005).
- [9] Y. Y. Wang et. al., Phys. Rev. Lett. **77**, 1809 (1996).
- [10] I. Ohana et. al., Phys. Rev. B. **40**, 2225 (1989).
- [11] J. P. Falck et. al., Phys. Rev. Lett. **69**, 1109 (1992).
- [12] R. Löwenich et. al., Phys. Rev. B **63**, 235104 (2001).
- [13] D. Salamon et. al., Phys. Rev. B **51**, 6617 (1995).
- [14] J. P. Hill et. al., Phys. Rev. Lett **80**, 4967 (1998).
- [15] P. Abbamonte et. al., Phys. Rev. Lett., **83**, 860 (1999).
- [16] M. Z. Hasan et. al., Science **288**, 1811 (2000).
- [17] A. Kotani and S. Shin, Rev. Mod. Phys. **73**, 203 (2001).
- [18] Y. J. Kim et. al., Phys. Rev. Lett. **89**, 177003 (2002).
- [19] L. Lu et. al., Phys. Rev. Lett. **95**, 217003 (2005).
- [20] E. Collart et. al., Phys. Rev. Lett. **96**, 157004 (2006).
- [21] L. Lu et. al., Phys. Rev. B **74**, 224509 (2006).

- [22] J. P. Hill et. al., J. Syn. Rad. **14**, 361 (2007).
- [23] Due to different energy calibration, the apparent incident energy scale in this work is different from that reported in Ref. [18]. Our incident energy was calibrated by measuring the absorption edge of Cu metal foil, which is located at 8980.5 eV according to Deslattes et al. [Rev. Mod. Phys. **75**, 35 (2003)]. As a result, the incident energy scale in this work is shifted by a constant amount of 1.5 eV when compared to that of Ref. [18], in which an edge energy of 8979 eV was used according to Bearden and Burr [Rev. Mod. Phys. **39**, 125 (1967)].
- [24] P. Kuiper et. al., Phys. Rev. Lett. **80**, 5204 (1998).
- [25] L. C. Duda et. al., J. of the Phys. Society of Japan **67**, 416 (1998).
- [26] G. Ghiringhelli et. al., Phys. Rev. Lett. **92**, 117406 (2004).
- [27] S. Tanaka and A. Kotani, J. of the Phys. Society of Japan **62**, 464 (1993).
- [28] S. Uchida et. al., Phys. Rev. B **43**, 794 (1991).
- [29] A. S. Moskvina, Phys. Rev. Lett **91**, 037001 (2003).
- [30] B. O. Wells et. al., Phys. Rev. Lett. **74**, 964 (1995).
- [31] S. Doniach, B. J. Roulet and M. E. Fisher, Phys. Rev. Lett. **27**, 262 (1971).
- [32] R. Neudert et. al., Phys. Rev. Lett **81**, 657 (1998).
- [33] T. Thio et. al., Phys. Rev. B **42**, 10800 (1990).
- [34] H. Y. Fan, Phys. Rev. **82**, 900 (1951).
- [35] H. Fröhlich, Phys. Rev. **79**, 845 (1950).